CONVERSION EFFICIENCY IN THE PRODUCTION OF SULFURIC ACID BY THE CONTACT PROCESS

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Thesis
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CONVERSION EFFICIENCY IN THE PRODUCTION OF SULFURIC ACID BY THE CONTACT PROCESS

A Thesis
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University for the degree of
Master of Science in Engineering

By

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BIOGRAPHICAL SKETCH

Ward Hanson Sachs, Jr. was born January 9, 1915 at Urbana, Illinois. He received his elementary and high school education in the public schools of Fayetteville, Arkansas, and Atlanta, Georgia. In 1936 he was graduated from the Georgia School of Technology with the degree of Bachelor of Science in Chemical Engineering. In June 1939 he was awarded the Master of Science degree from the University of Tennessee. He was employed by the Tennessee Copper Company, Copperhill, Tennessee, until July 1941 when ordered to active duty with the United States Navy. He served with the navy in the Atlantic, Mediterranean, and Pacific Theaters of Operation until June 1945 when he was ordered to the United States Naval Academy Graduate School and subsequently to Cornell University where he was enrolled in the Graduate School in November 1945 for training in Ordnance Engineering.

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CONVERSION EFFICIENCY IN THE PRODUCTION OF SULFURIC ACID BY THE CONTACT PROCESS

INTRODUCTION

The catalysts now used in the manufacture of sulfuric acid from sulfur dioxide by the contact process are either vanadium oxide or finely divided platinum deposited on a suitable carrier. Numerous investigators have studied the catalytic oxidation of sulfur dioxide with the objective of formulating equations to represent the reaction rate. The most recent contribution is the set of theoretical equations of Uyehara and Watson[10], who have correlated the data of Lewis and Ries[8] by an expression based on the theory of activated adsorption presented by Hougen and Watson[5]. This equation fits the experimental data of Lewis and Ries as well as their own empirical equation, and is here used in making comparisons of conversion efficiencies with varying load rates.

CONTACT PROCESS

The basic reaction for commercial production of sulfuric acid by heterogeneous catalysis is credited to Peregrine Phillips, who was issued a British patent in 1831 for the oxidation of sulfur dioxide by passing a mixture of sulfur dioxide and air through a hot platinum tube[3]. There was no really commercial application of the contact process for a long time after this. The chemical and engineering conditions for practical application of the contact process had not developed, the existing chamber process was adequate to supply the demand for acid of ordinary concentration, and there was very little demand for fuming sulfuric acid.

The discovery of synthetic methods for making alizarin from anthraquinone, in 1870, created a very active demand for fuming sulfuric acid. Since the manufacture of fuming acid from chamber acid is expensive and inefficient, this new demand resulted in renewed interest in the contact process. Partly because of the erroneous theory of Winkler that the reaction gases should be used in stoichiometric proportions, progress was very slow. Gradually, however, successful contact processes were developed. The early development was in Germany, and most of the early work was done by Badische Anilin-und Soda-Fabrik. For a long time the operating conditions were kept confidential; about 1900 the essential features of the process were disclosed and patents covering them were issued. Until 1927 the only practicable commercial processes used platinum as catalyst; in 1927 the use of vanadium in the non-exchangeable nucleus of non-siliceous base-exchange carriers developed by Jaeger and his associates was introduced to the commercial field.

The most successful platinum catalysts have been those carried on supports such as asbestos fiber, magnesium sulfate, and silica gel, these different types having become more or less identified with the particular process in which they are employed. The preparation of these catalysts, although simple in principle, is in practice something of an art. The process involves the wetting of the carrier with a solution of a platinum salt, usually platinic chloride, and then reducing the salt to metallic platinum. With platinized magnesium sulfate and platinized asbestos, about 5 to 6 troy ounces of platinum per daily ton of sulfuric acid are required[3]. This corresponds to a concentration of platinum of about 0.1 to 0.3 per cent in the magnesium sulfate mass as compared to 6 to 10 per cent of the weight in the asbestos catalyst.

Although the use of vanadium catalysts for the oxidation of sulfur dioxide was suggested as early as 1895, it was not until about 1927 that the introduction of Jaeger's improved catalysts placed vanadium masses in a position to compete commercially with the platinum catalysts. The vanadium masses are prepared by the deposition of salts of vanadium pentoxide on a carrier such as Kieselguhr[2]. The activity of the commercial catalysts is usually greatly increased by the addition of "promoters" such as potassium, calcium, and barium compounds. The mechanism of the oxidation reaction on these catalysts presumably involves the reduction of the vanadium to one of the lower oxides and the later re-oxidation to the pentoxide.

In the operation of any commercial process the most important factors which the engineer can control are temperature, pressure, ratio of reactants, catalyst, and time of contact. These controllable factors may affect either the equilibrium or the reaction rate. Temperature, pressure, and ratio of reactants may affect both the equilibrium and the rate of reaction; a catalyst can affect only the rate at which equilibrium is established. In determining the optimum operating conditions for a reaction it is necessary to analyze the problem both from a viewpoint of equilibrium yield and reaction velocity.

EQUILIBRIUM CONVERSION

Equilibrium yield can be computed from the familiar mass action relations. The reaction under consideration may be represented by the chemical equation:

$$SO_2 + 1/2\ O_2 = SO_3$$

The general mass-action equation for this reaction is:

$$K_p = \frac{p_{SO_3}}{\left[p_{SO_2}\right]\left[p_{O_2}\right]^{\frac{1}{2}}}$$

In the computation of the equilibrium yield or percentage conversion of SO_2 to SO_3 the following symbols are used:

a = Moles of SO_2 in original mixture.

b = Moles of O_2 in original mixture.

c = Moles of N_2 in original mixture.

x = Fraction of SO_2 in original mixture converted to SO_3 when equilibrium is reached.

P = Total pressure.

Basis: 100 moles of entering gas.

At equilibrium there will be:

	Moles	Mole Fraction	Partial Pressure
SO_2	$a(1-x)$	$\frac{a(1-x)}{M}$	$\frac{a(1-x)}{M}P$
O_2	$b-a/2x$	$\frac{b-(a/2)x}{M}$	$\frac{b-(a/2)x}{M}P$
N_2	c	$\frac{c}{M}$	$\frac{c}{M}P$
SO_3	ax	$\frac{ax}{M}$	$\frac{ax}{M}P$
Total	$a+b-\frac{ax}{2}+c$ moles $= M$		

The expression for the law of mass action may now be written in the form

$$K_p = \frac{\frac{ax}{M}P}{\left[\frac{a(1-x)}{M}P\right]\left[\frac{(b-\frac{a}{2}x)}{M}P\right]^{\frac{1}{2}}}$$

which reduces to $$\frac{1}{P}\left[\frac{x}{1-x}\right]\left[\frac{100-\frac{a}{2}x}{b-\frac{a}{2}x}\right]^{\frac{1}{2}} = e^{\left[\frac{22190}{RT}-\frac{19.15}{R}\right]} \qquad (1)$$

since $$K_p = e^{\left[\frac{22390}{RT}-\frac{19.55}{R}\right]}$$

This gives an expression for equilibrium conversion as a function of temperature and initial gas composition. If we specify the analysis of the original mixture we can compute the equilibrium conversion at any desired temperature. Figure (1) has been prepared from Equation (1) for three different gas mixtures. It indicates the theoretical percentage conversion that would be obtained if equilibrium were established in the system at the various temperatures. In commercial practice complete equilibrium is very seldom achieved because the length of time required for equilibrium to be reached would require equipment of prohibitive size. However, even when the reaction does not proceed to equilibrium in the available contact time, the operation may be commercially feasible if the approach to equilibrium is rapid.

REACTION RATE

Many of the factors influencing the equilibrium conversion also play an important role in determining the reaction rate. Sometimes a change that increases the rate of reaction reduces the extent of the conversion. For example, while the equilibrium conversion decreases from 99.2 per cent at 400° C. to 93.0 per cent at 500° C., the reaction rate at the higher temperature is approximately forty times that at the lower temperature[6].

The oxidation of sulfur dioxide is a reaction the rate of which can be greatly increased by the presence of a catalyst - usually either finely divided platinum or vanadium oxide. To arrive at a basis for equipment design, many investigators have studied this reaction with the purpose of formulating a mathematical expression for reaction rates.

The oxidation of sulfur dioxide on platinum catalysts has been extensively investigated by Bodenstein and

Fink[1], Knietsch[7], and Taylor and Lenher[9], and attempts have been made by these workers to correlate the results by empirical equations. As a result of experiments carried out at constant volume Taylor and Lenher proposed an equation of the form

$$-\frac{dx}{dt} = K'\frac{a-x}{(s+x)^{\frac{1}{2}}} \qquad (2)$$

in which "x" represents the pressure change in time, "t"; "a" is the oxygen pressure at the beginning of the experimental run minus the oxygen pressure at equilibrium, and "s" is one-half the sulfur trioxide pressure at the start of the run.

Grosvenor and Phillips[3] introduced the following symbols in applying Equation (2) to conditions of constant pressure and expressing quantities as moles per 100 moles of original unoxidized gas containing no sulfur trioxide:

X = Moles of SO_2 at any instant.

X_0 = Moles of SO_2 in original mixture.

X_e = Moles of SO_2 at equilibrium.

Z = Total number of moles of gas at the instant.

C = A factor to convert the pressure units of Taylor and Lenher into moles per 100 moles of original gas.

k = CK = "activity" of catalyst.

Substitution of the above nomenclature into Equation (2) produces

$$-\frac{dX}{dt} = \left(\frac{k}{\sqrt{Z}}\right)\frac{X-X_e}{\sqrt{X_0-X}}\ . \qquad (3)$$

Integration between limits X_1 and X_2 for the moles of sulfur dioxide present and treating the total number of moles of gas as a constant at its average value, Z_m, gives

$$Kt = \frac{1}{\sqrt{Z_m}}\Big[2\sqrt{X_0-X_1} - 2\sqrt{X_0-X_2} + \sqrt{X_0-X_e}\Big)\Big(\log_e\frac{\sqrt{X_0-X_e}+\sqrt{X_0-X_2}}{\sqrt{X_0-X_e}-\sqrt{X_0-X_2}} - \log_e\frac{\sqrt{X_0-X_e}+\sqrt{X_0-X_1}}{\sqrt{X_0-X_e}-\sqrt{X_0-X_1}}\Big)\Big]. \quad (4)$$

Except for the most critical work Z_m may be assumed to be 100, since the change in volume is relatively small. This equation has been recommended by Grosvenor and Phillips for computing approximate partial conversion obtained as a gas passes successively through several parts of a commercial converter.

If no sulfur trioxide is present in the initial gas mixture, since $(X_0 - X_1) = 0$, Equation (4) simplifies to

$$Kt = \frac{1}{\sqrt{Z_m}}\Big[\sqrt{X_0-X_e}\,\log_e\frac{\sqrt{X_0-X_e}+\sqrt{X_0-X_2}}{\sqrt{X_0-X_e}-\sqrt{X_0-X_2}} - 2\sqrt{X_0-X_2}\Big]. \quad (5)$$

The converting power of different catalysts may be evaluated in terms of a standard by this equation. Modification of conversion by variations in gas composition and flow rates can also be predicted. Such computations are facilitated by the construction of curves correlating the difference between equilibrium conversion and the obtained conversion with the "time activity" product, Kt, for a given temperature. However, computations with the above equations assume isothermal conversion; in most actual units the conversion is effected in adiabatic steps. Modifications must be introduced to make the equations apply to adiabatic conditions.

Moreover, the above expressions are based on experimental observations using platinum catalysts; strict applicability to other types of catalysts cannot be assumed.

In 1927, Lewis and Ries[8] investigated the reaction under conditions which more nearly approximated commercial practice, and attempted to correlate their data by an empirical equation. More recently, Uyehara and Watson[10] have developed a theoretical equation based upon the theory of activated adsorption which represents the experimental data of Lewis and Ries as adequately as does the empirical relation proposed by them.

The formulation of any theoretical equation for representing the rate of reaction in any chemical change must be postulated upon some mechanism for the reaction. There are many commercially important gas reactions, such as the one in question, which are known to occur more rapidly as heterogeneous processes on the surface of a solid catalyst than as a homogeneous gas phase reaction. It has been generally agreed that the primary function of the catalyst is to adsorb the reacting molecules and by so doing to reduce the activation energy required for the reaction[4]. Adsorption of gases by solids may fall into one of two types depending upon the nature of the forces involved: (a) Van der Waal's adsorption, in which the forces are of a physical nature; and (b) "Chemisorption" or activated adsorption, which involves forces of a nature similar to those involved in the formation of chemical bonds.

The mechanism of reactions occurring at the surface of a solid catalyst involves five steps:

(1) The mass transfer of the reactants from the main body of the gaseous mixture to the solid interface.

(2) Adsorption of the reactants on the surface of the catalyst.

(3) Reaction on the surface of the catalyst to form adsorbed products.

(4) Desorption of the reaction products.

(5) Mass transfer of the gaseous products from the surface to the bulk of the gas phase.

If any one of the consecutive steps takes place much more slowly than all of the rest, the slow reaction determines the overall reaction rate. By analysis of experimental data it is possible to eliminate certain of the possible steps as rate-determining in a particular process. For example, if the mass transfer of reactants or, more fundamentally, if diffusion were the rate-determining step, the temperature coefficient of the reaction rate would be of the same order as for gaseous diffusion. However, gaseous diffusion rates do not vary exponentially with temperature as do rates to heterogeneous chemical reactions but in proportion to the square root of the temperature.[4]

As pointed out by Hougen and Watson[5], the rates of these different steps depend upon widely different factors in addition to the concentration gradients involved. The steps involving mass transfer are controlled by the diffusivities of the particular gases present and the degree of turbulence in the flow system. The steps involving adsorption and desorption depend on the character and extent of the catalyst surface and the activation energies required for the adsorption and desorption of the components involved. The actual rate of the surface reaction depends upon the extent and character of the catalytic surface, insofar as it affects the activation energies required for the particular reaction. Hougen and Watson have developed theoretical rate equations based upon these concepts and on the reasonable assumption that one of the four steps may be regarded as rate controlling, and that the other steps are so rapid relative to the controlling rate that equilibrium will be reached with respect to them.

Uyehara and Watson[10] have applied the resulting equations to the reaction involving the catalytic oxidation of sulfur dioxide on the surface of a platinum catalyst. Their line of attack is based on the possibility of four rate-determining steps: activated adsorption of sulfur dioxide, activated adsorption of oxygen, and desorption of the sulfur trioxide. They assume that oxygen is atomically adsorbed on the catalyst, that one of the four steps controls the rate, and that the remaining steps are relatively so fast that they reach and maintain equilibrium. With these assumptions Uyehara and Watson have applied the theoretical relations of Hougen and Watson^5 to yield the following equations for each of the possible rate controlling steps: Adsorption of sulfur dioxide rate controlling,

$$r = \left(\frac{E_A C T e^{-\frac{\Delta H^{\circ\prime}}{RT}}}{1 + P_{O_2} K_{O_2} + \frac{P_{SO_3} K_{SO_2}}{\sqrt{P_{O_2}} K} + P_{SO_3} K_{SO_3} + P_{N_2} K_{N_2}} \right) \left(P_{SO_2} - \frac{P_{SO_3}}{\sqrt{P_{O_2}} K} \right). \quad (6)$$

Adsorption of oxygen rate controlling, similar to above.

Desorption of sulfur trioxide rate controlling,

$$r = \left(\frac{E_A C T e^{-\frac{\Delta H^{\circ\prime}}{RT}}}{1 + P_{SO_2} K_{SO_2} + \sqrt{P_{O_2}} K_{O_2} + P_{SO_2} \sqrt{P_{O_2}} K_{SO_3} K + P_{N_2} K_{N_2}} \right) \left(P_{SO_2} \sqrt{P_{O_2}} - \frac{P_{SO_3}}{K} \right). \quad (7)$$

Surface reaction rate controlling.

$$r = \left(\frac{E_A C T e^{-\frac{\Delta H^{\circ\prime}}{RT}}}{1 + P_{SO_2} K_{SO_2} + \sqrt{P_{O_2}} K_{O_2} + P_{SO_3} K_{SO_3} + P_{N_2} K_{N_2}} \right) \left(P_{SO_2} \sqrt{P_{O_2}} - \frac{P_{SO_3}}{K} \right). \quad (8)$$

The symbols are defined as follows:

r = reaction rate, moles/unit mass of catalyst/unit time.

E_A = effectiveness factor.

C = overall rate constant.

T = temperature degrees Kelvin.

ΔH = overall standard enthalpy change.

R = gas law constant.

K = overall fluid reaction equilibrium constant.

w = proportionality constant relating concentration change to reaction rate, r.

P_{SO_2}, etc. = partial pressure, atmospheres.

From a qualitative analysis of experimental data adsorption of sulfur dioxide as rate-controlling was eliminated as a possibility by the fact that the initial rate of oxidation was increased by an increase in partial pressure of either sulfur dioxide or oxygen, whereas Equation (6) would require that the initial rate of oxidation be reduced by the increased concentration of oxygen. The possibility of oxygen adsorption being rate controlling is eliminated similarly. Desorption of sulfur trioxide concentration is indicated by experimental data. Equation (8) for the rate of surface reaction was selected by Uyehara and Watson as best representing the qualitative trends observed in experimental data. The nitrogen concentration was shown by Bodenstein and Fink[1] to have no effect on the oxidation rate, so that in their final equation Uyehara and Watson have dropped out all terms involving the adsorption equilibrium constant of nitrogen. By letting

$$C_t = E_1 L T e^{\frac{-\Delta H''}{RT}} \quad \text{and} \quad d = 1 + \sqrt{P_{O_2} K_{O_2}} + P_{SO_3} K_{SO_3}$$

Equation (8) can be written

$$\sqrt{\frac{P_{SO_2}\sqrt{P_{O_2}} - P_{SO_3}/K}{r}} = P_{SO_2}\frac{K_{SO_2}}{\sqrt{C_t}} + \frac{d}{\sqrt{C_t}} . \qquad (9)$$

The adsorption constants are evaluated from experimental data. If the concentration of sulfur dioxide is varied while the other concentrations are held constant, a plot of $\sqrt{\frac{P_{SO_2}\sqrt{P_{O_2}} - P_{SO_3}/K}{r}}$ against P_{SO_2} will produce a straight line, the slope of which is $K_{SO_2}/\sqrt{c_t}$. By similar plots correlating partial pressures of oxygen and sulfur trioxide at the same temperature, the other constants, $K_{O_2}/\sqrt{c_t}$ and $K_{SO_3}/\sqrt{c_t}$ can be evaluated. By substituting values of the constants thus found in Equation (9) c_t can be evaluated by applying it to each experimental observation at the temperature under consideration.

Experimental data show that initial oxidation rate is directly proportional to the first power of the partial pressure of sulfur dioxide, and a plot of Equation (9) produces a straight line the slope of which is almost zero. Thus the term $P_{SO_2}K_{SO_2}$ in the denominator of the rate equation is negligible in comparison to the other terms and in the final equation is omitted.

Uyehara and Watson's final equation takes the following form:

$$\frac{r}{\omega} = \left[\frac{E_1 C T e^{-\frac{\Delta H''}{RT}}}{\left(1+\sqrt{P_{O_2}K_{O_2}} + P_{SO_3}K_{SO_3}\right)^2}\right]\left[P_{SO_2}\sqrt{P_{O_2}} - \frac{P_{SO_3}}{K}\right] \qquad (10)$$

and they recommend the use of the following constants:

$$K_{SO_3} = e^{\frac{21400}{RT} - \frac{23}{R}}$$

$$K_{O_2} = e^{\frac{20360}{RT} - \frac{23}{R}}$$

$$K = e^{\frac{22490}{RT} - \frac{19.75}{R}}$$

$$\Delta H'' = +3690$$

The quantity wE_AC for the particular catalyst in use must be evaluated from experimental observations. By employing the above equation the value of the combined term r/wE_AC can be computed for any temperature and composition of gas. Curves presented in Figure (2) represent such computations based on an initial gas composition of 7.8 per cent SO_2, 10.8 per cent O_2, and 81.4 per cent N_2. In this case the logarithm of $(r/wE_AC) \times 10^4$ has been plotted against the fraction of sulfur dioxide in the original mixture converted to sulfur trioxide.

USE OF EQUATIONS

If the constants w, E_A, and C have been evaluated for a catalyst, the use of the rate equation permits the determination of the volume of catalyst required for securing a specified conversion at a known rate of feed. As shown by Hougen and Watson[5], in an elementary cross section of catalyst bed having a volume dV if a conversion dX is produced, it necessarily follows from the definition of reaction rate, r, that $FdX = rp_b dV$, where F is the reactor feed rate in moles per unit time, X is the moles of SO_2 converted per mole in the initial feed, p_b is the bulk density of the catalyst, and V is the volume of the reactor. As shown in Figure (2), r = f(X) so that we have $dV = \frac{FdX}{p_b f(X)}$, which upon integration gives the volume of the reactor

$$V = \frac{F}{Pb}\int_{X_1}^{X_2} dX/f(X) \qquad (11)$$

Conversion data are commonly expressed in terms of space velocity, S_v, which may be defined as volumes of feed, measured at standard conditions, per unit time per unit volume of catalyst. Space velocity can be obtained from Equation (11) since

$$S_v = \frac{FM_f}{Vp_f} = \frac{p_b M_f}{p_f \int_{X_1}^{X_2} dX/f(X)} \tag{12}$$

where M_f is the average molecular weight of the reactor feed and p_f is the density of the feed at standard conditions. Evaluation of the integral may be accomplished by graphical methods.

Even though the constants w, E_A, and C have not been evaluated for the catalyst in use, the rate equation makes possible the comparison of conversions at different flow rates and the prediction of conversions that may be expected for different rates of feed. This merely involves the evaluation of the integral $\int_{X_1}^{X_2} dX/f(X)$ under the two conditions. For example, a gas mixture which contained initially 7.8 per cent SO_2, 10.8 per cent O_2, and 81.4 per cent N_2 has passed through a preliminary converter in which conversion has proceeded to the extent of 50 per cent is to be introduced into an isothermal converter at 400° C. for final treatment at a rate such that S_v equals 900 cubic feet per hour per cubic foot of catalyst and leaves the converter at a composition corresponding to a conversion of 96 per cent. It is desired to determine the conversion which could be expected with the same converter if the space velocity were increased to 1200 cubic feet per hour per cubic foot of catalyst. For this type of problem it is convenient to plot cumulative values of the integral versus fraction converted, as shown in Figure (3). Then it is only necessary to read from the chart the desired conversion corresponding to the value of the integral. In the example, letting X_2 be the required conversion we have from Equation (12)

$$S_v = \frac{P_b M_f}{p_f \int_{0.50}^{0.96} dX/f(X)} \quad \text{and} \quad S'_v = \frac{P_b M_f}{p_f \int_{0.50}^{X_2} dX/f(X)} \quad .$$

Combination of these equations gives

$$\int_{0.50}^{X_2} dX/f(X) = \frac{S_v}{S'_v} \int_{0.50}^{0.96} dX/f(X) \quad .$$

From curve "A", Figure (3) $\int_{0.50}^{0.96} dX/f(X) = 72.0$ and we

have $\int_{0.50}^{X_2} dX/f(X) = \left(\frac{900}{1200}\right)(72.0) = 54.0.$

Again from Figure (3) we find that the conversion corresponding to this value for the integral is 93.2 per cent.

In an adiabatic converter, the temperature, and therefore the reaction rate, varies from point to point. By the application of a heat balance it is possible to express the temperature as a function of the fraction of sulfur dioxide converted and further to define the reaction rate as a function of temperature. To illustrate let us suppose that a burner gas having 7.8 per cent SO_2, 10.8 per cent O_2, and 81.4 per cent N_2 has passed through a preliminary converter and that 50 per cent conversion has resulted. After cooling, the gas enters an adiabatic converter at 400° C. at a space velocity of 1200 cubic feet per hour per cubic foot of catalyst and a conversion of 80 per cent is obtained. It is desired to determine to what rate the space velocity must be reduced to obtain a conversion of 90 per cent. We shall assume a mean heat capacity for the gas mixture throughout the range of temperature involved of 7.2 gram calories per gram mole per degree C. ΔH for the reaction will be taken as 22,500 gram calories per mole. In order to make the computed values for temperatures corresponding to fractions of sulfur dioxide converted fall upon the isotherms previously plotted in Figure (2), conversions required to produce temperature rises, Δt, of 25, 50, 75, and 100° C. will be computed. Taking 100 moles gas mixture containing 3.9 per cent SO_2, 8.85 per cent O_2, and 81.4 per cent N_2, we have

$$\Delta t = 22500(x)/(7.2)(100) \text{ or } x = 720\,\Delta t/22500,$$

where x is the number of moles of SO_2 converted in the adiabatic reactor. Then the total fraction of SO_2 converted in both preliminary and final converter will be

$$X_A = (3.9 + 720\ \Delta t/22500)/7.8$$

Substituting in this equation values for Δt we find that X_A has the following values at the temperatures indicated:

	400° C	425° C	450° C	475° C	500° C
X_A	0.50	0.62	0.71	0.81	0.91

By drawing the broken curve through the isotherms on Figure (2) corresponding to these points we obtain a curve correlating the reaction rate and conversion efficiency for the adiabatic conversion. Using this curve as our function for the reaction rate we may again by graphical integration evaluate the integral $\int_{0.50}^{X_2} dX/f'(X)$ for adiabatic conditions and as has been done for the isothermal case plot the cumulative values of the integral against fractional conversion. This appears as curve "B", Figure (3). From this curve we find that for a conversion of 80 per cent the integral $\int_{0.50}^{0.80} dX/f'(X)$ has a value of 14.3 and the value corresponding to 90 per cent conversion is 18.4. Inserting these values in the equation

$$\int_{0.50}^{0.90} dX/f'(X) = \frac{S_v}{S'_v}\int_{0.50}^{0.80} dX/f'(X)$$

we have $18.4 = \frac{1200}{S'_v}(14.3)$ and the desired space velocity,

$S'_v = \frac{14.3}{18.4}(1200) =$ 932 cubic feet per hour per cubic foot of catalyst.

SUMMARY

The increased demand for high strength sulfuric acid brought about by the synthesis of dyestuffs resulted in the introduction of a new process for the manufacture of sulfuric acid involving heterogeneous catalysis. There have been constant improvements in the process arising from improvements in design and control which had their basis in the fundamental thermodynamic and kinetic properties of the chemical reaction. Experimental investigation by numerous workers has produced empirical and theoretical relations which can be used as a tool in the design of equipment and in determining optimum conditions of operation. This paper has illustrated the manner in which reaction rates can be used in predicting conversion in the contact process for sulfuric acid production.

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APPENDIX

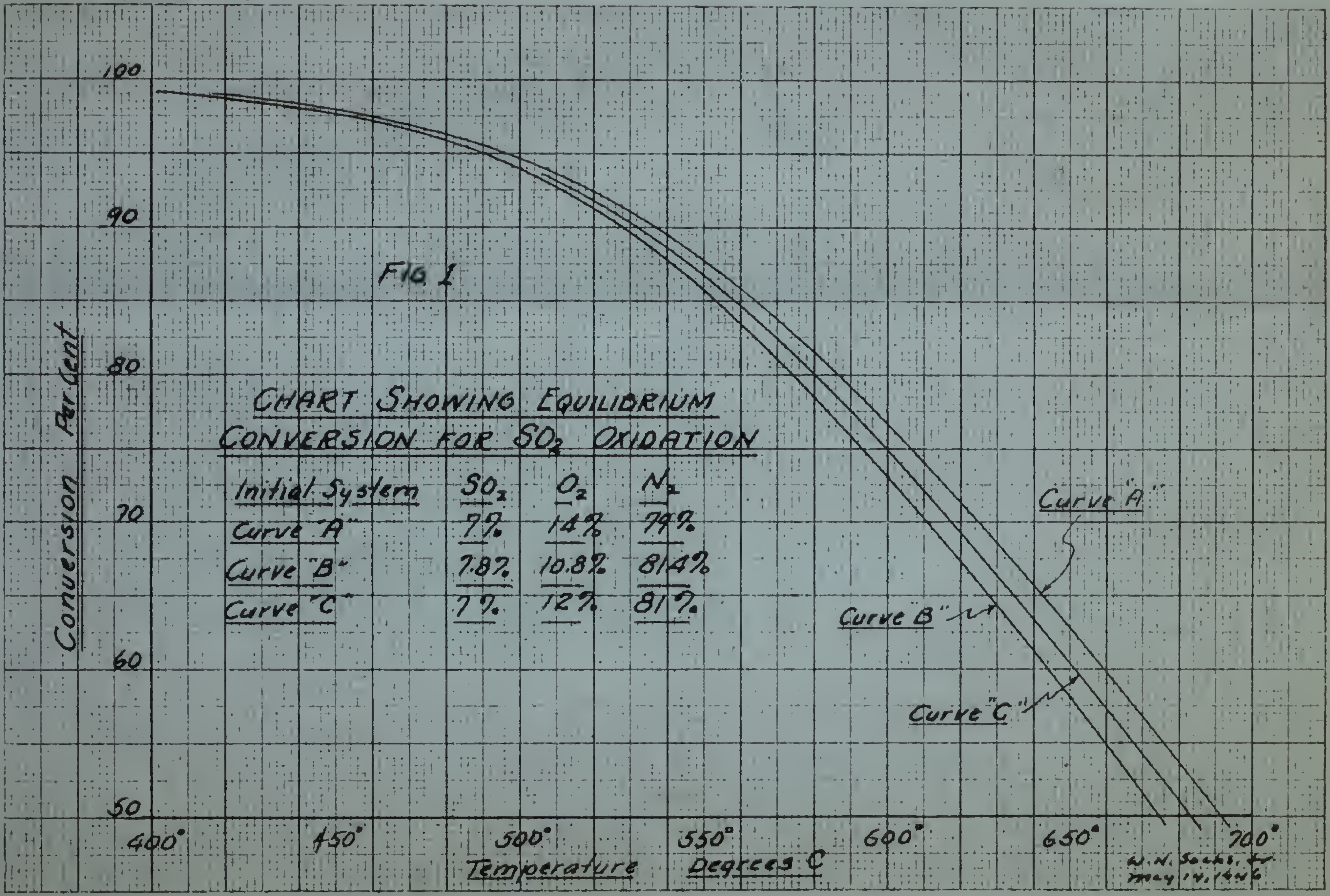

FIG 1

CHART SHOWING EQUILIBRIUM CONVERSION FOR SO_2 OXIDATION

Initial System	SO_2	O_2	N_2
Curve "A"	7%	14%	79%
Curve "B"	7.8%	10.8%	81.4%
Curve "C"	7%	12%	81%

W. N. Sachs, Jr.
May 14, 1946

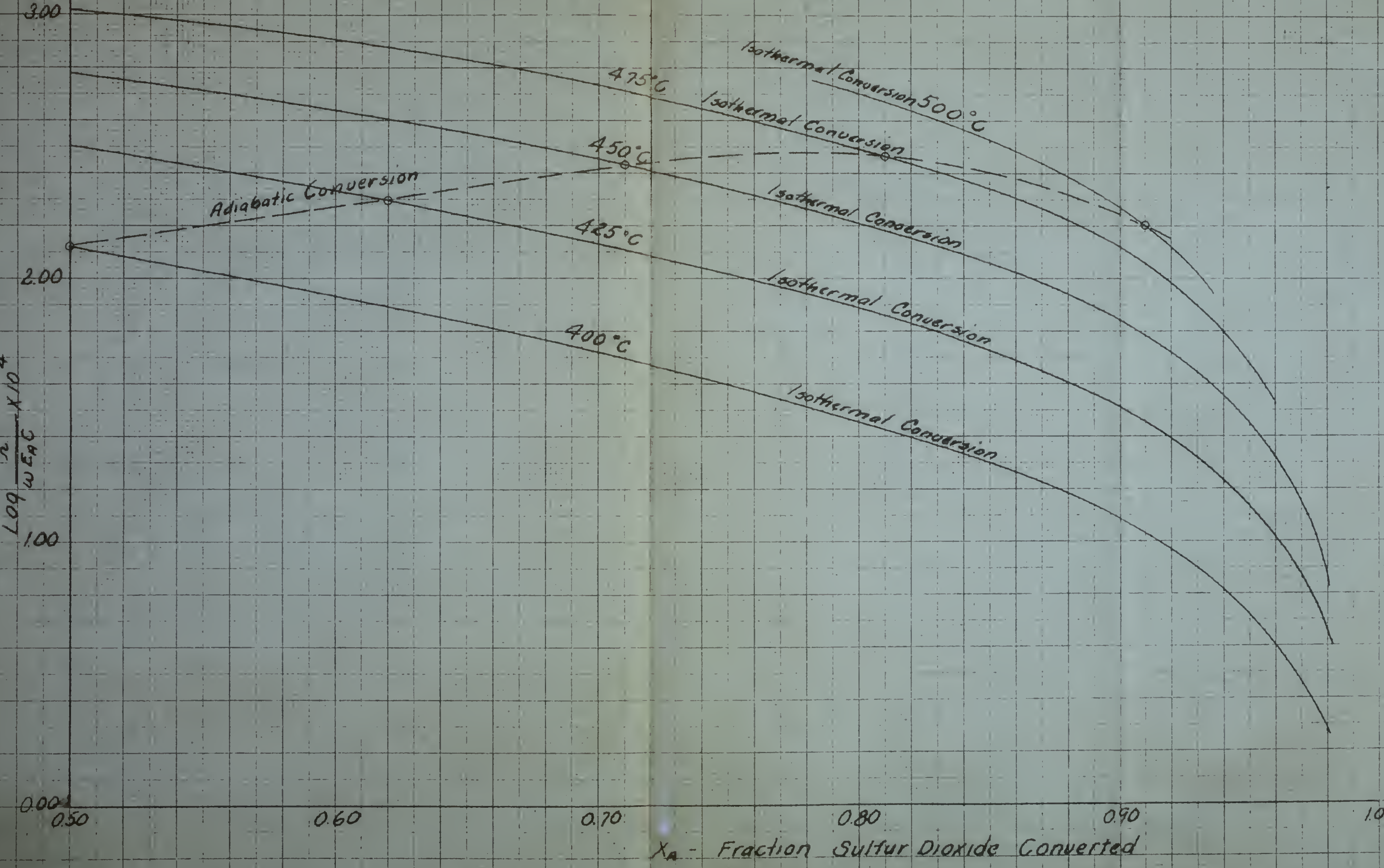

FIG. 2

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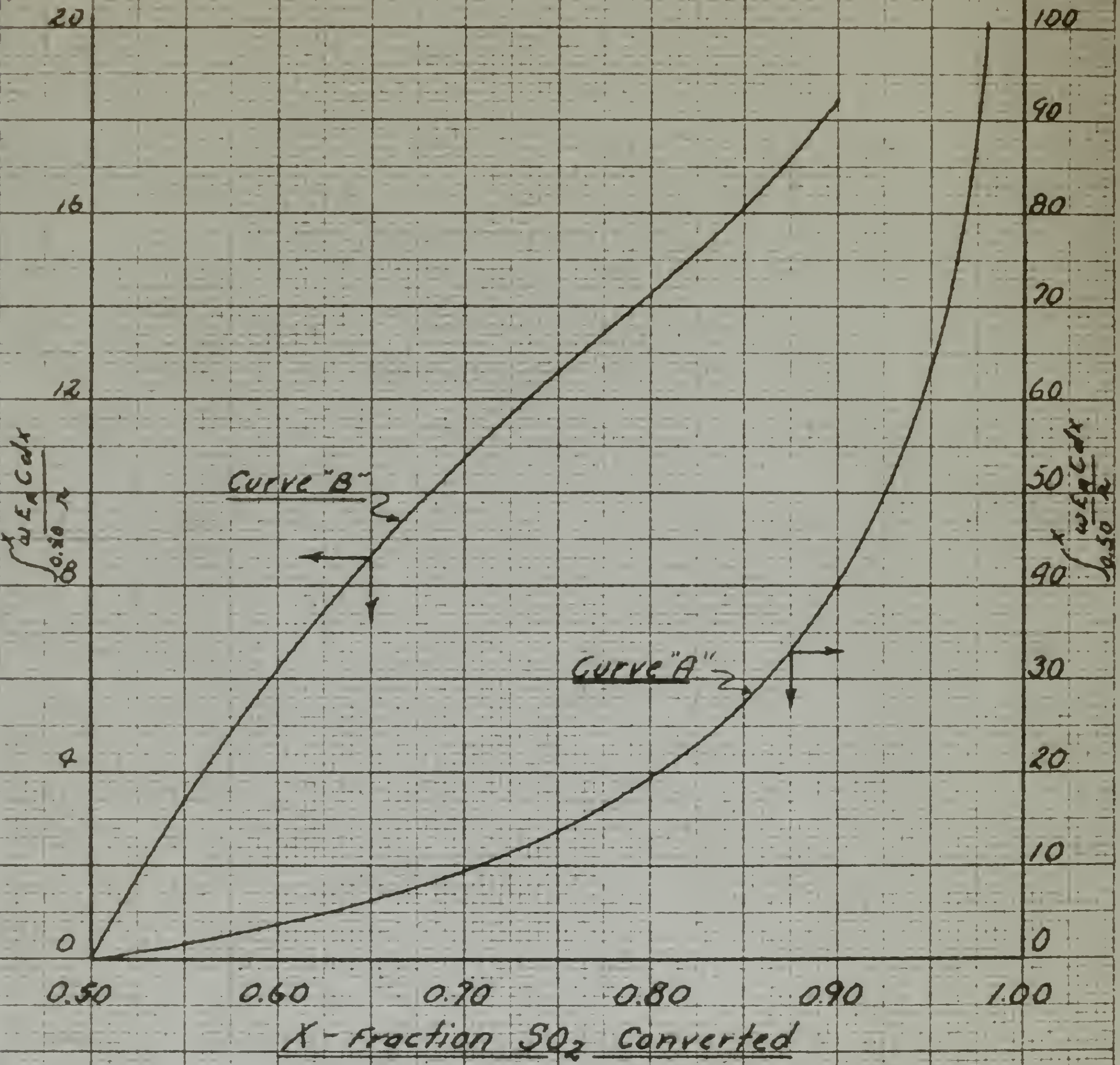

Curve "A" for Isothermal Conversion

Curve "B" for Adiabatic Conversion

CUMULATIVE VALUES FOR $\int_{0.50}^{x} \frac{\omega E_A C\,dx}{R}$

W. H. Sachs Jr.
May 14, 1946

FIG. 3

DATE DUE

Thesis 7864
S15 Sachs
Conversion efficiency
in the production of
sulfuric acid by the
contact process.

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Conversion efficiency
in the production of
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